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Final Report

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ABSTRACT: This report documents a demonstration project conducted at McAlester Army Ammunition Plant in Oklahoma. The technology is based on anaerobic bacteria which attack dissolved explosives such as TNT and RDX at the nitro groups, converting them to amino groups. Once the explosives are transformed, they become amenable to aerobic degradation. This process functions as a pretreatment for the pinkwater, after which the effluent is discharged to an aerobic treatment plant and mixed with the rest of the plant's wastewater. The bacteria are cultivated on granules of activated carbon contained in a fluidized bed. The demonstration equipment controlled the conditions to maintain favorable conditions for anaerobic bacteria through control of temperature, pH, and nutrients. Fuel grade ethanol was used as the substrate to maintain the bacterial population. The results show that this technique can be successful and less costly than the existing granular activated carbon adsorption process.

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Conversion Factors

Non-SI* units of measurement used in this report can be converted to SI units as follows:

Multiply	By	To Obtain
degrees Fahrenheit	(5/9) x (°F – 32)	degrees Celsius
feet	0.3048	meters
gallons	0.003785412	cubic meters
gallons per minute	3.785	liters per minute
inches	0.0254	meters
pounds	0.4535924	Kilograms

*_Système International d'Unités_ ("International System of Measurement"), commonly known as the "metric system."

Acronyms and Abbreviations

AAP	Army Ammunition Plant
2-ADNT	2-amino-4,6-dinitrotoluene
AMC	Army Materiel Command
BOD	biological oxygen demand
CERL	Construction Engineering Research Laboratory
COD	chemical oxygen demand
DNT	dinitritoluene
DoD	Department of Defense
EPA	Environmental Protection Agency
ERDC	Engineer Research and Development Center
ESTCP	Environmental Security Technology Certification Program
FBR	fluidized bed reactor
GAC	granular activated carbon
GAC-FBR	granular activated carbon-fluidized bed reactor
gpm	gallons per minute
JMC	Joint Munitions Command
kgal	1,000 gallons
mg/L	milligram per liter
NPDES	National Pollutant Discharge Elimination System
O&M	operation and maintenance
PLC	programmable logic controller
PVC	polyvinyl chloride
sCOD	soluble chemical oxygen demand
TAT	triaminotoluene
TNB	trinitrobenzene
TNT	trinitrotoluene
TSS	total suspended solids
µg/L	microgram per liter
WWTP	wastewater treatment plant

Preface

This study was conducted for the Environmental Security Technology Certification Program (ESTCP) under Project 2000 of FY2004, and was further supported by the D048 Program under Project 4A162720D048. The ESTCP Program Manager for Compliance is Dr. Robert Holst and the ESTCP Director is Dr. Jeffrey Marqusee.

This work was performed by the Environmental Processes Branch (CN-E) of the Installations Division (CN), Construction Engineering Research Laboratory (CERL). The study was performed in part by personnel from McAlester Army Ammunition Plant (AAP) and Retec, Inc., under contract to CN-E. In addition to funds received from ESTCP, the Joint Munitions Command supplied funds for facilitation and enclosure of the operating system at McAlester AAP. The CERL Principal Investigator was Dr. Stephen W. Maloney. The associated Technical Director was Gary W. Schanche. Dr. Kirankumar Topdurti is the Chief, CN-E; and Dr. John Bandy is Chief, CN. Dr. Alan Moore is the Director of CERL.

CERL is an element of the U.S. Army Engineer Research and Development Center (ERDC), U.S. Army Corps of Engineers. The Commander and Executive Director of ERDC is COL James R. Rowan, EN, and the Director of ERDC is Dr. James R. Houston.

1 Introduction

Background

The production, handling, and demilitarization of conventional munitions yield wastewaters (commonly referred to as pinkwater) contaminated with energetic materials that are regulated under discharge permits at Army Ammunition Plants (AAPs). The accepted method for removal of these energetic compounds is adsorption onto activated carbon. This treatment is expensive and yields a secondary waste stream of spent activated carbon that has to be handled as a hazardous waste. The Construction Engineering Research Laboratory (CERL) has been evaluating alternative methods of treatment which will be less expensive and avoid the generation of a secondary hazardous waste such as spent activated carbon.

The compounds of interest which must be removed from wastewaters generated at load, assemble, and pack facilities such as McAlester AAP include 2,4,6 trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and 1,3,5-trinitrobenzene (TNB). The compounds are highly resistant to aerobic degradation and have been found to persist in aerobic environments for more than 50 years, based on studies of groundwater contamination at formerly used defense sites. The presence of the nitro groups on the ring structures makes these compounds relatively immune to electrophilic attack by aerobic bacterial populations.

CERL developed a two-step biodegradation process that used an anaerobic treatment step to first convert the target compounds into their reduced analogs (e.g., TNT is converted to triaminotoluene [TAT]), and then an aerobic step to mineralize the resulting compounds. This process was studied at the laboratory bench scale to demonstrate the pathways of conversion, at the pilot scale to establish loading factors and critical control parameters, and finally, in the study reported here, at the demonstration scale, in which a near full-scale system was designed and tested by CERL and contractors from EFX Systems, Inc. (who later moved to Retec, Inc.). The system was then turned over to the operators at McAlester AAP to demonstrate that it could treat the wastewater as produced on their facility.

This report covers the operation of the system, the operational problems that were encountered, and the results obtained after the system achieved stable operation. A

Cost and Performance Report on this project, maintained on the Environmental Security Technology Certification Program (ESTCP) site, can be found at: http://www.estcp.org/documents/techdocs/200004.pdf.

Objectives

The overall objective of this demonstration was to transfer a new technology for the treatment of pinkwater to operators at an AAP. Several sub-objectives were to determine the acceptability of the operating systems to personnel at McAlester AAP, demonstrate that the system can endure shutdowns that occur for several reasons (e.g., electrical outage during severe weather), demonstrate the system's ability to remove the target compounds without replacing the granular activated carbon (GAC), and determine the costs of operation.

Approach

Before the operation started, results of previous pilot tests were presented to officials responsible for the regulation of McAlester AAP's wastewater discharge. The presentation was made to personnel of the Oklahoma Department of Environmental Quality, and permission was granted to conduct the study.

The system was constructed offsite, and the major components of the system were shipped to McAlester AAP. EFX Systems personnel installed the system in an existing building, and connected the system to influent and effluent tanks for the test program. The system was then turned over to the operators at McAlester AAP. Technical support was provided over a 2-yr period to resolve problems in the design. This system was the first of its kind to be installed for the purpose of anaerobic transformation to be followed by aerobic treatment in the existing wastewater treatment plant (WWTP). Records were kept for both the treatment levels reached at the anaerobic fluidized bed reactor (FBR) and the final treatment at the existing WWTP after combination with the other sources of wastewater at McAlester AAP.

Scope

The techniques described in this report apply to AAPs, which produce wastewater contaminated with TNT, RDX, HMX, TNB, and similar compounds. The goals of developing and implementing new technologies for munitions wastewater are addressed.

Mode of Technology Transfer

The results of this study will be presented at Department of Defense (DoD) and engineering conferences and meetings. Facility tours are available upon request if suitable arrangements/ clearances can be obtained. The Cost and Performance Report is available at the web address listed in the earlier Background section. Several papers detailing the results of studies leading up to this demonstration have been published and are covered in Chapter 2, **Literature Review**.

This report will be made accessible through the World Wide Web at the URL: http://www.cecer.army.mil

2 Literature Review

Nitrated organic compounds in wastewater streams at DoD facilities are the result of manufacture and demilitarization of explosives. These nitrated organics are recalcitrant to biological degradation due to the presence of highly oxidized nitro groups on the aromatic ring. The electron-withdrawing effect of the nitro groups inhibits electrophilic attack by oxygenase enzymes (Bruhn et al. 1987). This degradation becomes more difficult as the number of nitrosubstitutions increases (Spain 1995). Compounds such as TNT and RDX, therefore, have a long persistence in the natural environment. Spanggord et al. (1991) demonstrated complete degradation of 2,4 dinitrotoluene (DNT) by a *Pseudomonas sp.* with stoichiometric ratios of nitrite released. Although oxygenase-based degradation of nitrosubstituted organics occurs, for the more highly substituted compounds such as TNT and RDX, the initial step in biodegradation in the natural environment appears to be a reduction of the nitrosubstituted group to the corresponding amine under both aerobic and anaerobic conditions. This rate-limiting step can be highly accelerated under strictly anaerobic conditions (VanderLoop et al. 1998).

The anaerobic granular activated carbon – fluidized bed reactor (GAC-FBR) for nitroaromatic compounds has been under development for several years by CERL, in conjunction with the University of Cincinnati and EFX Systems, Inc. Initial work was performed on propellant wastewater containing dinitrotoluene (Maloney et al. 1998; VanderLoop et al. 1998). Success with dinitrotoluene extended the research to TNT, RDX, and pinkwater (Adrian and Sutherland 1998; VanderLoop et al. 1998; Hwang et al. 2000).

Development of the two-step, anaerobic-aerobic treatment for nitrated explosives began with investigations of propellant wastewater. The propellant wastewater contained DNT and relatively high concentrations of ethanol. The author observed that flow tests for DNT treatment on GAC yielded much greater capacity than predicted from isotherm studies (Maloney et al. 1995). Laboratory testing showed that the DNT could be converted to diaminotoluene (DAT) in the first step under anaerobic conditions, and that the DAT was then easily treated in an activated sludge reactor under aerobic conditions (Berchtold et al. 1995). A pilot test of this process (Maloney et al. 1998) showed that it could operate under highly variable influent concentrations found under field conditions. Further laboratory study was then directed at the constituents of pinkwater.

VanderLoop et al. (1998) demonstrated that TNT can be transformed into compounds amenable to aerobic mineralization in a laboratory reactor. Hwang et al. (2000) demonstrated the sequential conversion of the nitro-groups to amino-groups in TNT degradation, and Adrian and Sutherland (1998) demonstrated the degradation of RDX under anaerobic conditions. In a previous pilot test, the ability of the anaerobic GAC-FBR process to consistently reduce the concentration of total nitrobodies to below 100 µg/L in pinkwater was observed (Maloney et al. 2002).

Initial pilot testing at McAlester AAP demonstrated the ability of the anaerobic GAC-FBR to produce an effluent with less than 100 µg/L total nitrobodies on a consistent basis. Results from one test period from a pilot test conducted for pinkwater are presented in Table 1. During this test period, TNT concentrations in the feed averaged 29.2 mg/L. The only other nitrobody detected was 2-amino-4,6 DNT, which was detected only once at 8.7 mg/L. No nitrobodies were detected in the system effluent; all were below the 0.03 mg/L detection limit. The removal efficiency for chemical oxygen demand (COD) averaged 77.4 percent. The ratio of applied electron donor to TNT during this period averaged 27.8 mg COD/mg TNT. The TNT loading rate averaged 0.34 kg/m^3-d.

Current practice to control contamination from pinkwater requires adsorption of the TNT and RDX onto GAC. This process is expensive (approximately $100/kgal for pinkwater compared to the Army Materiel Command [AMC] average of $2/kgal for industrial wastewater [Dept. of the Army 1995]), and produces a byproduct hazardous waste in the spent activated carbon. Anaerobic processing of pinkwater and other nitroaromatic containing wastewaters appears to be a reliable, cost-effective treatment option.

Table 1. Performance of a pilot GAC-FBR (9/19–10/1/98).

Parameter	Units	Influent	Effluent	% Removal
TNT	mg/L	29.2 (9.8)	<0.03	>99.9
RDX	mg/L	<3.0	<0.03	--
HMX	mg/L	<3.0	<0.03	--
TNB	mg/L	<3.0	<0.03	--
2-amino-4,6 DNT	mg/L	<3.0*	<0.03	--
sCOD**	mg/L	902 (156)	198 (35)	78.0
TSS	mg/L	13 (9)	22 (16)	--

*Detected in one sample at 8.7 mg/L
**Includes added ethanol (sCOD = soluble COD)
OLR = 9.3 kg COD/m^3-d
TNT LR = 0.34 kg/m^3-d
Flow = 1.5 gpm
HRT = 125 min
Temperature = 90 °F
TSS = total suspended solids
Values shown as Average (Standard Deviation)

3 Process Description

The pilot GAC-FBR consists of a fluidized bed of activated carbon granules in a cylindrical reactor (see Figure 1). The FBR was a 4.5-ft (1.4-m) diameter column with an overall height of 22 ft (6.7 m) and a bed of GAC occupying approximately 11 ft (3.4 m) when expanded. Water was recirculated through the column continuously at approximately 220 gpm (830 L/min) to keep the GAC fluidized, and pinkwater for treatment was pumped into the recirculation line. Nutrients and co-substrate (electron donor) were also fed into the recirculation line. The nutrient solution consists of nitrogen, phosphorus, and several trace nutrients and minerals listed in Table 2. The nutrient solutions were fed from two reservoirs, with the bulk of the materials in one reservoir, and the calcium and manganese salts in a second reservoir. Separation into the two reservoirs was necessary to avoid precipitation of compounds that formed when all nutrients were mixed together.

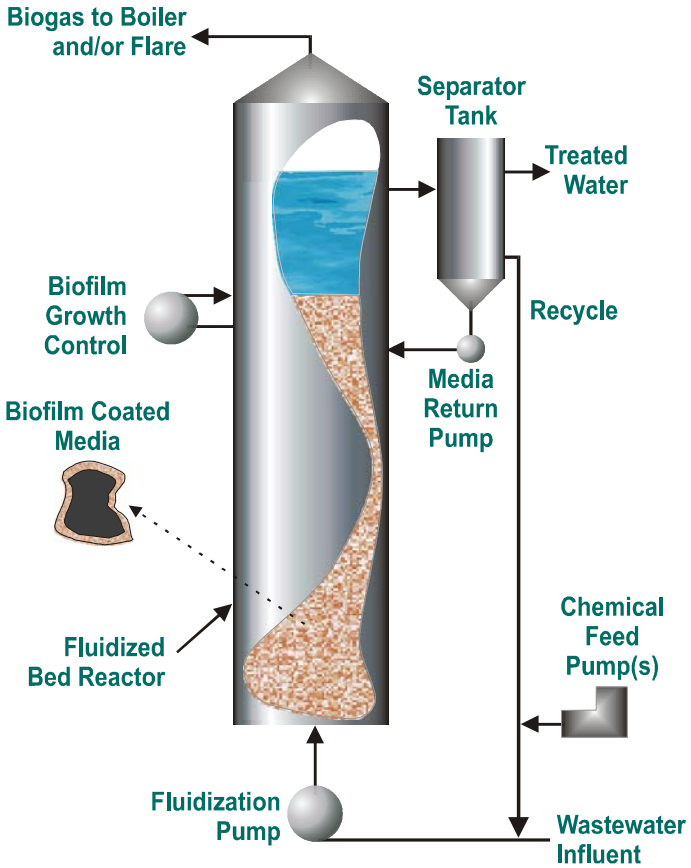

Figure 1. Conceptual drawing of an anaerobic granular activated carbon – fluidized bed reactor.

Table 2. Trace nutrients and minerals.

Component	Source
Magnesium	$MgCO_3 \bullet 6\ H_2O$
Manganese	$MnSO_4$
Potassium	KCl
Calcium	$CaCl_2 \bullet 2\ H_2O$
Iron	$FeCl_3 \bullet 6\ H_2O$
Cobalt	$CoCl_2 \bullet 6\ H_2O$
Nickel	$NiCl_2 \bullet 6\ H_2O$
Boron	H_3BO_3
Copper	$CuCl_2$
Molybdenum	$NaMoO_4 \bullet 2\ H_2O$
Sulfur	$MnSO_4$

In addition to the nutrients and co-substrate, sodium hydroxide was injected into the feed solution as needed to control the pH. The pH was controlled using a probe in the recirculation line connected to a programmable logic controller (PLC). The system was designed to operate with a pH set point of 6.8 to 7.0, and when the pH in the reactor dropped below that range, a solution of sodium hydroxide (20 percent) was injected into the system until the pH reached the top of the range. Controlling pH is critical to maintaining favorable conditions for the anaerobic bacteria, and has presented a problem in small-scale reactors used at laboratory scale. The use of the automated control system has eliminated this control problem in pilot- and full-scale systems.

The influent water was heated prior to injection in the recirculation line via heat exchange with the effluent from the system. The system was designed to be operated at 95 °F to provide favorable conditions for the anaerobic bacteria. The recirculation pumps also added heat to the system. Additional heat was added to the system using a heat exchange loop around the separator. The heated side of the system was maintained at 180 °F, and a valve would open to allow water in the recirculation loop around the separator through the heat exchanger. When the temperature in the system reached its set point, the valve would direct the water to a pipe that bypassed the heat exchanger and returned the water to the separator.

The GAC-FBR process has two removal mechanisms that are operative. Biological degradation is the principal mechanism of contaminant removal. The GAC acts primarily as a support medium for the attachment and growth of bacteria that form biofilms. However, the adsorptive capacity of the GAC provides a second benefit in that it can cut off peaks of influent concentration through adsorption, and later desorb the contaminants when the bacteria have reduced the aqueous phase concentration. This allows the bacteria to work at a relatively steady-state mass removal,

and the GAC functions to buffer the aqueous phase concentration. This is particularly important in industrial operations, because the influent concentrations tend to vary widely.

As the bacteria develop into a biofilm on the GAC, the net density of the biofilm-coated GAC decreases. The particles with the greatest biofilm buildup migrate to the top of the fluidized bed. A biofilm growth control is used to gently shear the excess biomass off of the GAC particles at the top of the bed. The particle then becomes more dense and migrates back lower into the bed (shown on the left side of Figure 1). If the control fails to capture all of the particles, they then pass out to the separator tank, where they settle out. This provides a second opportunity to gently shear the biofilm off of the particle as the flow enters the separator tangentially, setting up a cyclonic flow. The GAC and residual attached biofilm are sent back to the column by a media control pump (shown on the right side of Figure 1).

Gas produced as a by-product of anaerobic degradation is collected at the top of the column, and sent to a flare to burn off the methane. It can also be vented to the atmosphere. For work inside an AAP, venting is the preferred method because of a prohibition on open flames.

This system does not use specialized bacteria. Instead, anaerobic bacteria from local sources, such as an anaerobic digester at a municipal WWTP, are used as the initial inoculum. The biomass is then grown in the reactor by feeding nutrients and co-substrate only to the point that gas production becomes significant, and then feeding the wastewater, starting at approximately 10 percent of design flow and slowly increasing as long as methane production is maintained.

The process tested at McAlester AAP was based on results of the previous pilot test. During the pilot test, the GAC-FBR had been successful in treating the explosives contaminants in the pinkwater when the mass loading of TNT was 0.22 kg TNT/m^3-day. The average production of pinkwater had been 7.5 gpm. The demonstration was designed to operate at this level, although the operating level of the existing pinkwater plant is approximately 50 gpm.

The TNT concentrations experienced in pilot demonstration test ranged up to 80 mg/L, and had an average of approximately 40 mg/L. The overall design of the system was based on treating the average flow at the peak concentration (i.e., 7.5 gpm at 80 mg/L TNT). During the demonstration test, the activity at McAlester AAP increased compared to the years during which the pilot test was conducted. This increase resulted in higher flows and, more importantly, higher TNT concentrations that often remained above 100 mg/L for weeks at a time.

The use of the GAC-FBR was justified based on reduced operating costs. The pilot results had compared the costs of operating the existing carbon adsorption system to the capital and operating costs of GAC-FBR. Capital costs for the existing system were left out of the comparison because the overall cost of a new system would have to be less than the operating costs of an existing system to justify replacing it.

Additional and more detailed information on the costs of two systems may be found in a companion publication, Cost and Performance Report on the ESTCP website. This report goes beyond the operating period used for the Cost and Performance Report and incorporates data from a period when most of the operating problems had been solved.

4 Demonstration Site

McAlester AAP was chosen as the demonstration site and was a full partner in the ESTCP proposal that funded the demonstration. McAlester AAP was the site of the pilot demonstration reported on elsewhere, and provided two important fixed facilities that greatly enhanced the operation of the demonstration. First, McAlester AAP collects all of its pinkwater generated to a central point, where it is stored in an influent basin. Second, McAlester AAP has an existing aerobic WWTP that receives the treated pinkwater, which allowed the demonstration team to insert the GAC-FBR into the process stream without extensive additional facilities.

Figure 2 shows a plan view of the demonstration site. An existing road bisects the site, and all facilities to the north (to the right in the figure) of the road were part of the existing pinkwater treatment plant, and all facilities on the south side of the road were installed either during the demonstration, or as part of the previous pilot test.

The demonstration plant consisted of a 4.5-ft diameter GAC-FBR, and a control skid which included a separator to remove carbon particles and other solids from the water being recycled. Pinkwater was taken after pressure filtration and stored in two influent tanks shown at the top of the plan view. Pinkwater was then sent to the control skid, where it was mixed with the recycle water, nutrients, and co-substrate (ethanol), and then pumped to the GAC-FBR. The recycle water was pumped into the bottom of the reactor through an array of nozzles, and the effluent flowed over a weir to the effluent pipe which went to the separator. Carbon particles with heavy amounts of attached biomass could flow out of the reactor, so the separator was used to recover these particles. The flow to the separator was introduced on the side to use turbulent circular flow to remove the excess biomass from the carbon particles. The carbon particles were then pumped from the bottom of the separator back to the GAC-FBR.

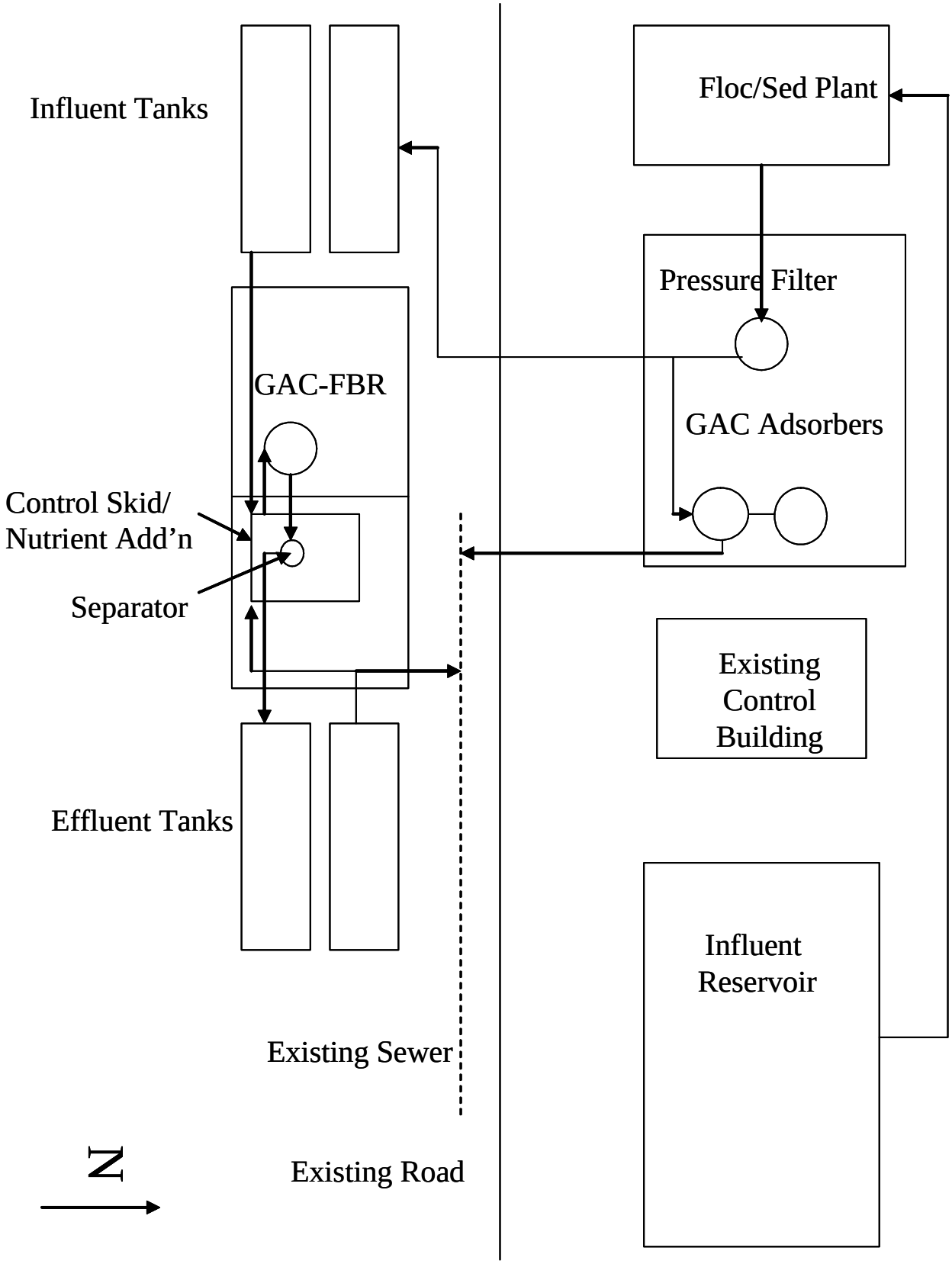

Figure 2. Demonstration site schematic (plan view).

The original demonstration plan placed the separator on the control skid, and the control skid was placed inside the building constructed for the pilot demonstration. The GAC-FBR reactor was too large to fit into that building, so it was placed outside on a concrete pad. A result of this design was that the top of the separator was well below the top of the GAC-FBR, and flow controls were added to keep the separator from overflowing or becoming drained. The overflow resulted in wastewater flowing out of the system through the effluent transfer barrel (described below). If the separator became drained, it could leave the recycle pump running in a cavitation mode, as there would be no water in the recycle line. Subsequent to the original design, McAlester AAP constructed a building completely around the GAC-FBR, eventually enclosing it.

Control of the water level in the separator was maintained by a modulating valve on the effluent line from the GAC-FBR. The Figure 3 schematic is a front view of the GAC-FBR and separator. Water in the GAC-FBR would flow over a weir inside the reactor and flow to an effluent pipe that went to the separator. The modulating valve would open up or pinch off flow to maintain a certain level in the effluent return line. The water level in the separator was determined primarily by the level of the overflow port, which sends effluent to the barrel on the control skid. If the modulating valve allowed too much water into the separator, however, it could overflow too quickly. Conversely, if the flow were too restricted, the separator could be drained by the recycle pump that draws from a port on the separator. If that occurred, the recycle pump (not shown in Figure 3) would suffer cavitation damage as it drew air into the system.

Balancing the water levels in the effluent recycle line and the separator proved to be difficult during the demonstration. The level in both systems was measured by a pressure transducer, protected by a screened fitting called a “snubber.” The snubbers became fouled, giving very sluggish response and, in the case of the separator, the pressure transducer was giving inaccurate water level readings due to a vapor lock somewhere in the effluent gas lines. These problems will be further discussed in Chapter 5, **Operating Results**.

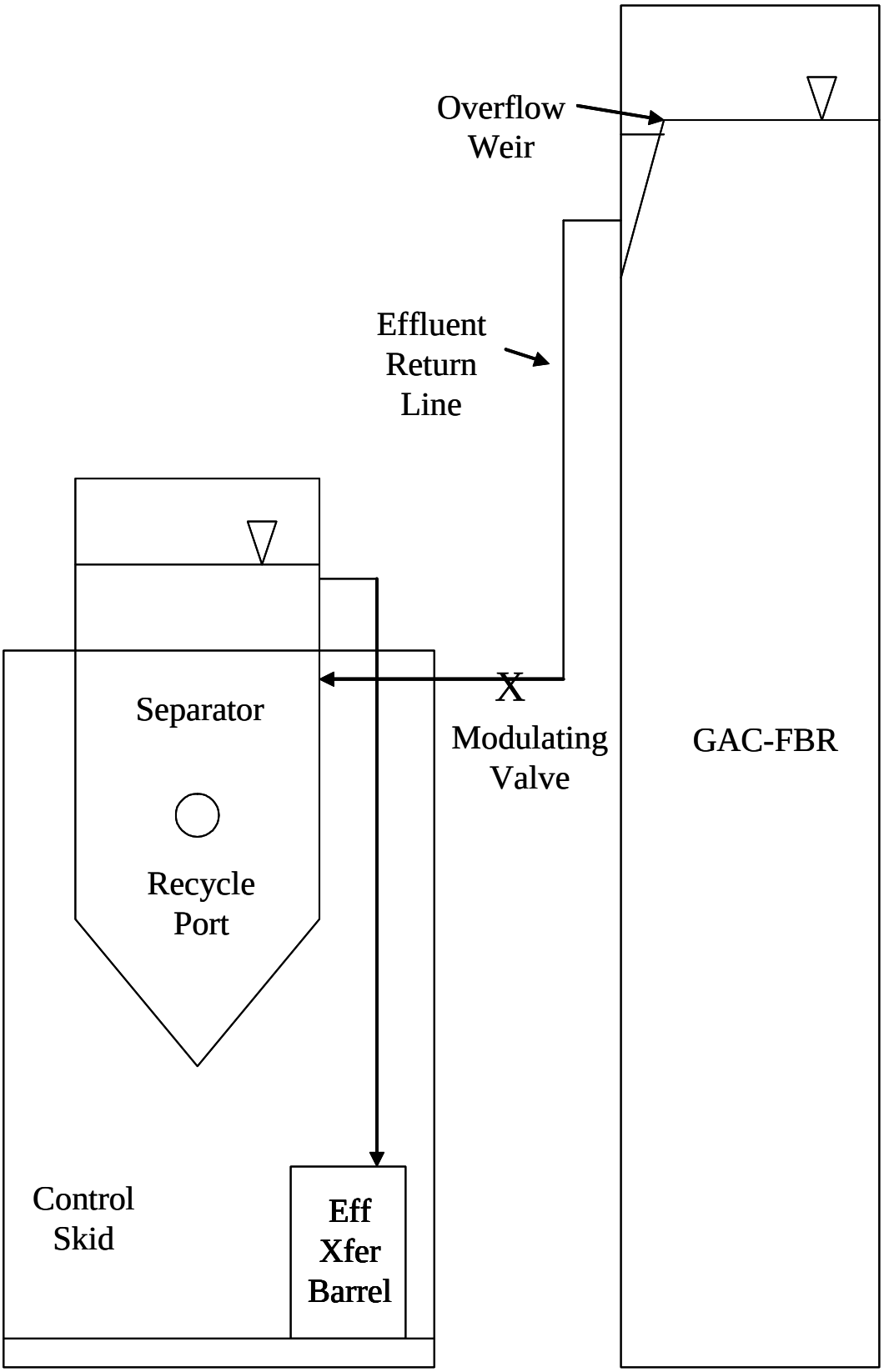

Figure 3. Schematic of hydraulic grade lines (elevation view).

Effluent from the separator flowed into a ground level barrel that was used as an effluent transfer tank. When the barrel reached a preset level, the effluent would be pumped to the effluent tanks for storage until the water could be analyzed for residual TNT, RDX, and by-products. When the barrel reached a preset lower level, the control skid would direct the effluent through a loop that contained a heat exchanger, and then the effluent would return to the barrel. The heat exchanger was used to recover residual heat and pre-heat the influent as it arrived at the control skid from the influent tanks. The effluent barrel and associated pre-heater caused several problems to the operation that will be discussed later in Chapter 5. As can be seen on the schematic in Figure 3, however, the effluent barrel was at the lowest hydraulic level, and could easily be overflowed by the separator if the modulating valve was not maintaining a steady level in the effluent return line.

Effluent stored in the bottom tanks shown in Figure 2 was piped back into the control skid building prior to disposal into the sewer. However, the piping was also designed to allow the recycle of the effluent to the influent pump on the control skid. This setup allowed water in the effluent tanks to be retreated if necessary, and also supplied a large source of water for recycle if there were operating problems within the system.

A holding pond between the demonstration plant and the existing aerobic WWTP allows for equalization of flow, and will allow the easily assimilated materials to mix with the rest of the wastewater and be partially treated. Part of the demonstration was to ensure that no excess loads were placed on the existing WWTP and, for that reason, biological oxygen demand (BOD) and nitrogen and phosphorus compounds were monitored at the existing WWTP.

5 Operating Results

Background

This chapter details the operating problems encountered during the demonstration test, the solutions found, and recommendations for future installations. This chapter does not address the treatment results, which will be addressed in Chapter 6. Rather, this section will deal mostly with mechanical and electrical problems that the operators encountered during the demonstration.

A principal objective of this demonstration was to show that operators at an AAP could accept this technology and operate it with limited maintenance. Although the technology developers and technology vendors may be very confident of the systems reliability, it will be commercially acceptable only when it can be incorporated into normal operations.

This system was the first of its kind to operate with the objective of anaerobically transforming pinkwater contaminants so that they could be treated in an aerobic WWTP. Fluidized bed reactors for biological processes have been used in a variety of installations for other purposes. This system, however, was designed for a relatively recalcitrant set of contaminants (e.g., TNT and RDX), which required the development of an acclimated biomass that could endure significant changes in concentration over short periods of time.

This was also the first time an anaerobic GAC-FBR system was designed to operate at several different hydraulic grade lines. The original design was to keep the separator inside a building, as it is much smaller than the GAC-FBR and would be more likely to freeze than the reactor if a prolonged, cold shutdown occurred. Because the existing building was not tall enough to house the GAC-FBR, the separator was installed on the control skid. The effluent transfer barrel was installed at an even lower level.

Most of the system operated from a single touchscreen, although there were also manual actuators to turn pumps on. The heating system had a separate operating panel and power supply with emergency shutoff. The only purpose of the heating system was to keep the hot side of the heat exchanger at a set level of 180 °F, and the heater control panel had a PLC with temperature readout for this purpose.

The system was not started by turning one switch. First, recycle flow had to be started by turning on the recycle pump at the touchscreen. Then the effluent transfer pump had to be turned on, followed by the feed pump, the co-substrate and nutrient pumps, and the caustic and heater loop pumps. When the system started to operate outside of process control parameters (e.g., temperature or pH), the PLC would switch the system into "cold shutdown," which would keep recycle going, but shut down feed flow. As long as the nutrients and co-substrate were operating in automatic mode, they would shut down whenever the feed shut down. If the system started operating outside of hydraulic parameters (e.g., separator level too high or low), the system would go into cold shutdown, where essentially everything but the heater was shut off (including the recycle pumps).

In addition to a multi-step process for starting the flow into the GAC-FBR, a process of slowly starting the influent flow was adopted after cold shutdowns. The collapse of the bed and refluidization may dislodge significant amounts of attached bacteria on the GAC, so instead of jumping directly to design capacity, the system would be restarted at 2 gpm. The flow would be increased once bioactivity was demonstrated by the generation of methane gas.

Initial Startup

The problem generated by multiple hydraulic grade lines was evident from initial startup. When hydraulically testing the system with clean water, the effluent transfer barrel overflowed whenever the system shut down. This resulted from the water that was stored in the effluent recycle line (see Figure 3 for a schematic representation). When the system shut down, the water would flow into the separator, and then overflow into the effluent transfer barrel. Although this barrel had a clamped on lid with a flexible gasket seal, it was insufficient to contain the water pressure, and water would shoot out at the location of a hinged joint.

The reason this occurred was that there was no shut-off valve on the effluent recirculation line. As a result, another valve controller was installed so that, whenever the system was put into cold shutdown, the valve on the effluent recycle line would shut completely.

Although some other glitches in the computer program were found during the initial startup, most problems arose during prolonged operation. The computer program problems were related to display registers being improperly formatted and calculations being off by a factor of ten. As operation continued over more than a year, some changes were added to the computer program operating the touchscreen to make it easier for the operators to work through the various screens displayed.

Operational Problems

Long-term operational problems were encountered due to the buildup of solids in the influent preheater heat exchanger, deposition of precipitates on metal surfaces of some pipes, and biological buildup in the air handling system. As a result of these operational problems, system changes were made to maintain operation. In one case, a system change was made to keep the system operational, although the underlying cause of the problem was not identified.

The piping system consisted of both bare steel and polyvinyl chloride (PVC). Bare steel was used in the influent feed line, influent preheater line/effluent discharge, and the main heater line. The main lines used for GAC-FBR effluent recycle from the top of the reactor to the separator, and from the separator through the recycle pumps back to the GAC-FBR, were all made of PVC.

After the system had been acclimated to the pinkwater and run for several months, the effluent discharge pump reached a point where it could not keep up with a feed rate above 5 gpm. The effluent transfer barrel would overflow when the effluent pump could not keep up with the influent pump. This overflow was first thought to be occurring because the pump was operating near the limits of its design, and the addition of the effluent storage tanks added 15 ft of head (when they were approaching full levels) for the pump to work against. The design of the pump had not included that extra 15 ft because it was planned for direct disposal to the sewer. A new pump with a greater capacity was purchased and installed.

When the pump was installed, however, the system was opened, revealing development of large precipitation on the bare steel surfaces. These precipitates would also be passed through the influent heat exchanger, which was designed to recover heat from the effluent before discharge. Eventually, the larger pump was also unable to keep up with the influent flow. As a result, the influent pre-heater was abandoned, and the flow was routed around it in flexible plastic hoses.

Analysis of the precipitates showed significant amounts of aluminum in the deposits. During the operation of the demonstration plant, McAlester AAP had been demilitarizing explosives containing tritanol — a composition that includes TNT and aluminum powder. This type of munition had not been handled during the pilot demonstration, and there were far fewer bare steel pipes in the pilot unit. The PVC pipes had no apparent deposition of precipitates that could be examined, so this problem seems to be limited to the bare steel. As a result, future systems should use PVC to the greatest extent possible, and limit bare steel to situations where the water quality is controlled, such as the hot water side of the main heat exchanger.

Precipitation also affected the readings coming from pressure transducers. These were protected by a "snubber," a small fitting that contained a fine screen. The screen became clogged with the same material that attacked the bare steel, which resulted in a very sluggish response to large pressure changes. In this case, a second, larger fitting was added which contained a diaphragm that would isolate the water in the pressure transducer from the wastewater being treated.

The slow response of the pressure transducers was one of several problems which contributed to the level of water in the separator operating out of prescribed bounds and requiring significant operator intervention to restart the system when it went into warm shutdown.

The pressure transducer on the effluent recycle line was used to maintain a constant level in the recycle line. When the pressure built up, indicating that the water level in the influent line was rising, the modulating valve would open to let the water flow out more quickly. Conversely, when the pressure on the transducer was getting low, the valve would throttle down the flow. If these reading responses were too slow, the valve could remain too restricted for a period long enough for the recycle pump to drain the separator, tripping the system to cold shutdown and shutting off the recycle pump along with all other pumps.

An operator would then be required to restart the system. Prior to restarting the system, water would have to be added to the separator to raise the level to within the acceptable operating range. During the demonstration, the acceptable range was 35-in. wide, so this meant that the pressure transducer was responding very slowly. At one point, a new snubber and a fitting containing a diaphragm to protect the new snubber from metal deposition were added to the system. This improved operation, but did not completely eliminate the problems with the separator tripping the plant for being either too high or too low.

A second problem with the separator level was discovered late in the demonstration. Figure 4 is a schematic diagram of the separator with the effluent, solids return line, and gas sampling system shown. The effluent line would overflow only as long as the influent pump was running, then the water level should drop below the bottom of the effluent pipe. The effluent pipe went down below the water surface at all times except when the water in the separator was very low. The gas collection lines were connected on both sides of the effluent line, however, so a siphon should not occur.

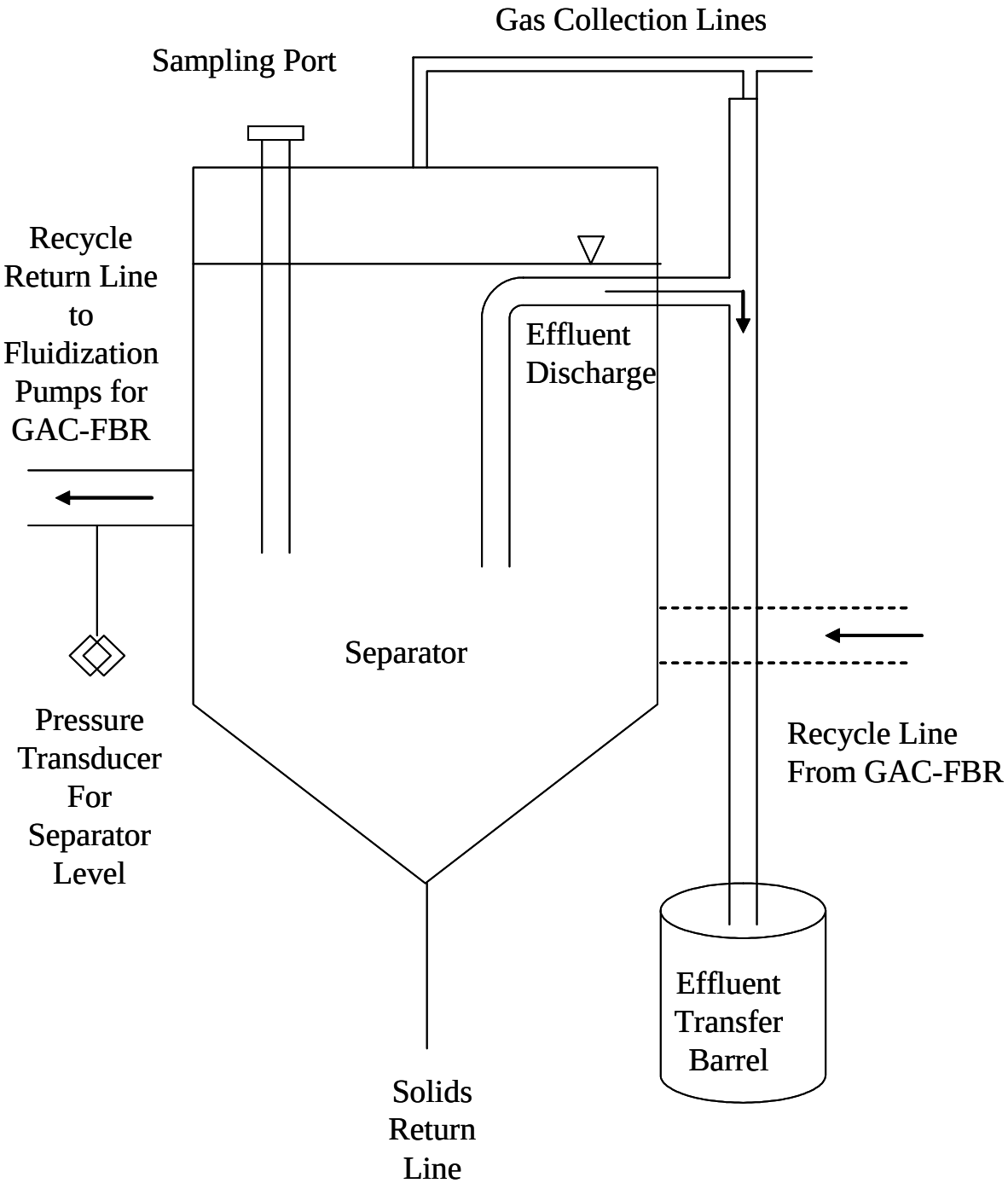

Figure 4. Schematic diagram of separator with sample and effluent ports.

The water level in the separator was determined by a pressure transducer on the recycle line that went from the separator through the fluidization pumps back to the GAC-FBR. This transducer was also protected by a snubber, which became clogged and gave sluggish responses. However, the use of the pressure transducer led to other problems that were not discovered until late in the demonstration. The effluent gas passed through a gas collection pipe, through a moisture removal tank and

then a flow meter, to be discharged outside the building. Two ports on this gas collection pipe were connected to an infrared gas analyzer to measure methane content. This gas collection pipe became clogged, severely restricting air flow.

As a result of the restricted flow, the pressure transducer was reading not only the pressure from the water level, but any excess pressure or reduced air pressure found in the separator. If the gas lines were clogged, the gas pressure could be depressed whenever the effluent transfer barrel discharged, because the contents of that barrel were being pumped out by the effluent transfer pump at a rate much greater than the influent rate. Similarly, gas production, as well as the increase in water level in the effluent barrel as it refilled, could increase the pressure inside the separator.

When the inside pressure was below atmospheric, the pressure transducer would give a false low reading on the water level, which would cause the system to shut down due to a low water level. Any build-up of gas pressure in the separator and associated gas lines would lead to false high readings in the separator, again causing the plant to shut down. The original 1/2-in. diameter metal pipes used for the gas collection system from the separator to the outside were replaced with 1-in. diameter PVC in August 2003. Problems with false readings from the pressure transducer still existed, however, and the reason for the vapor lock in the gas collection lines was never determined fully.

The problem of false readings was overcome by leaving the sampling port on the separator slightly open. The sampling port was a 4-in.-diameter pipe that went from the top of the separator to beneath the water surface, so the majority of the gas would not escape through that port. The port was sealed with four bolts and a rubber gasket. It was maintained slightly open by placing a cloth glove between the top fitting and the rubber seal to allow the separator to equalize to atmospheric pressure regardless of clogs in the gas collection line.

This solution has allowed the system to run without the problems of the separator shutting it down frequently. However, McAlester AAP is designing a construction change for the GAC-FBR system that will move the separator to the same hydraulic grade line as the top of the GAC-FBR. This move will overcome the false readings problem without relying on flow controls in the recycle line and pressure transducers.

Main Heating System

Several problems were encountered with the main heating system used to deliver hot water to the heat exchanger. The first problem occurred with a mercury displacement switch that was used to turn power on and off. The heating system would turn on any time the hot water temperature dropped below a set point (set at 180 °F). During the summer months, the heater would raise the temperature above the set point so quickly that the mercury displacement switch was moving back and forth too rapidly, leading to its failure. This problem was corrected by changing the set-point operation, in which a five-degree range was put into the system allowing the hot water to drop to 177 °F before the heater elements were turned back on, and remain on until the hot water reached 180 °F.

A second problem was never completely solved. The heating system had nine elements on nine different fuses, but the fuses were blowing very rapidly. This system was not unique to this demonstration and was unrelated to the technology being tested. During the first episode of rapid fuse loss, the heating system was removed, and returned to the vendor (Watlow, St. Louis, MO) for testing. The heating system was replaced by a smaller unit used during the pilot demonstration, and the problem had occurred in the summer so the smaller unit was sufficient. No problems were found in the heater, and it was returned and reinstalled. The problem of short fuse life continued, however. Watlow later indicated that a similar problem had been experienced elsewhere when the connecting wiring was less than 10-ft long. That was also the case at McAlester AAP, and the theory was that the wire was transmitting heat back to the fuses, which made them blow even when the current draw was below the fuse rating.

No solution to this problem has been determined. McAlester AAP is planning to run a steam line to the heat exchanger so the electric heater will no longer be required.

Operation Summary

Several design weaknesses were encountered that caused substantial problems with the operation of the system during the demonstration. Most of the problems have been solved as described above, or a secondary solution, such as maintaining the air pressure at atmospheric on the top of the separator by keeping a sampling port slightly open, has been implemented. No solution has been found for the relatively short fuse life, but that is being addressed by monitoring the fuses more regularly and by the plan to replace the electric heater with steam heat.

One problem scenario that had not been proposed for testing in the original plan was frequent collapse of the fluidized bed. Once the recycle flow shut down, the GAC would settle and collapse from a fluidized state to a compacted state. This change could lead to bacteria bridging across individual particles and clogging up the bed. It was also a concern for the fluidization nozzles, which could become clogged with GAC. However, the problems occurring due to the separator, which led to numerous shutdowns, showed the GAC-FBR to be relatively robust with respect to shutdowns. No bed clogging was observed during the demonstration, despite numerous shutdowns.

Another problem never anticipated was the GAC-FBR overheating. During one shutdown episode, a less experienced operator was called to restart the system. Unable to do so from the touchscreen, the operator used manual controls to get the system running again. Unfortunately, the heater loop was turned on manually also, continuously heating the system overnight, reaching 135 °F by the next morning. This caused methane production to drop to zero, and there was concern that the system had been "pasteurized," killing most of the bacteria. This was not the case, and the system did not have to be reseeded and re-acclimated to the feed because the bacteria recovered quickly. If anything, this episode seems to have made the bacteria more efficient after surviving the high temperatures.

One concern in the planning of this demonstration was the effect of allowing the bed to collapse on the fluidization nozzles at the bottom of the reactor. A set of air valves was installed on the bottom of the reactor so that pressurized nitrogen could be used to blow accumulated GAC out of the distribution system nozzles if they became clogged after a bed collapse. Operating experience showed that this concern was unfounded, because no problems were encountered in refluidizing the bed, despite having many periods of cold shutdown.

6 Treatment Process Results and Discussion

Effectiveness of treatment was judged by removal of the principal contaminants, TNT and RDX, from the influent wastewater. The analytical method used for these compounds, the U.S. Environmental Protection Agency (EPA) Method 8330 (U.S. EPA, 1996) also determined HMX, TNB, and 2-amino-4,6,dinitrotoluene (2-ADNT). HMX is a contaminant in RDX and is sometimes present at detectable quantities. TNB is a degradation product of TNT and 2-ADNT. Only TNT, RDX, and TNB were found in the influent at measurable concentrations during the demonstration. HMX and 2-ADNT were occasionally seen in the influent, but were not found in the effluent.

The results reported here represent a longer period than found in the Cost and Performance Report (ESTCP 2003). The main reason for the extended operation was to gain additional experience with the system under constant operating conditions. The data here represent all operations from September 2001 through the end of January 2004. The final 5 months represent continuous operation after the problems discussed above were addressed.

This additional operational period also allowed evaluation of the system with much higher TNT concentrations. The operating period used in the Cost and Performance Report (ESTCP 2003) ended in August 2002. Up to that point, the highest concentrations observed were around 80 mg/L. The extended operating period, however, showed concentrations in excess of 120 mg/L, which is 50 percent greater than the system design.

The results of the tests are shown in Figures 5, 6, and 7, for TNT, RDX, and TNB, respectively. The results for RDX are presented on a different scale than TNT. In general, RDX was less than 6 mg/L, although higher concentrations were experienced for brief periods in early 2003. Although RDX loadings were lower than TNT, RDX is more difficult to degrade. Adrian et al. (2003) demonstrated degradation rates for RDX to be at least an order of magnitude slower than TNT in a mixed culture of anaerobic micro-organisms. Close inspection of the chart will show that RDX did break through the reactor at two points. One was in a period of sporadic operation in November 2002, and another occurred during operational problems in

July 2003. The last 5 months have not shown any breakthrough of RDX, after most operational problems had been fixed or circumvented.

The results for TNB are shown in Figure 7, again on a different scale, as it was not found at concentrations as high as RDX. No problems were encountered with TNB removal during this demonstration.

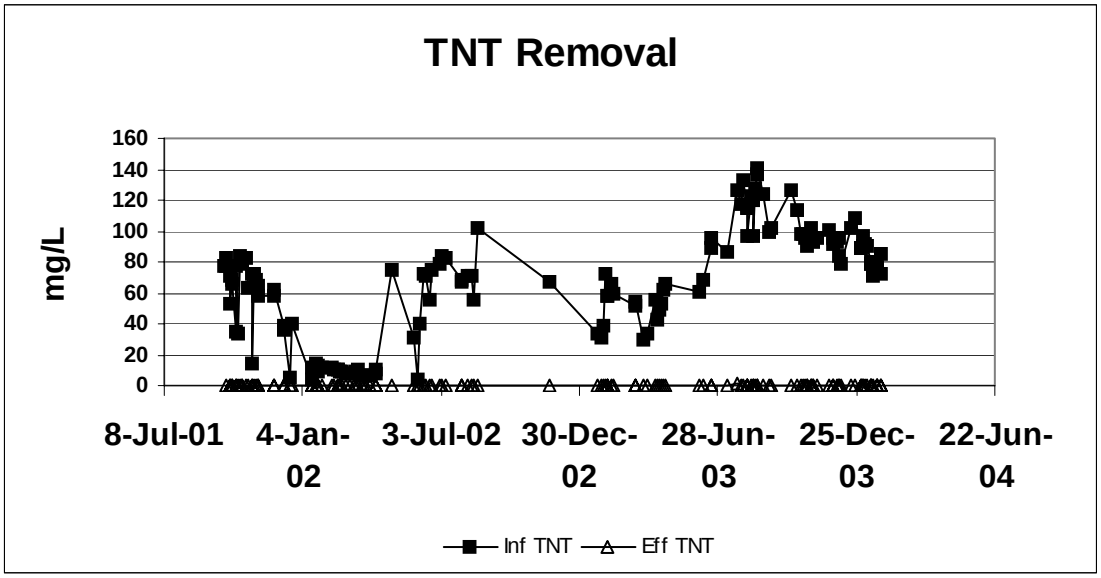

Figure 5. Influent and effluent TNT concentrations.

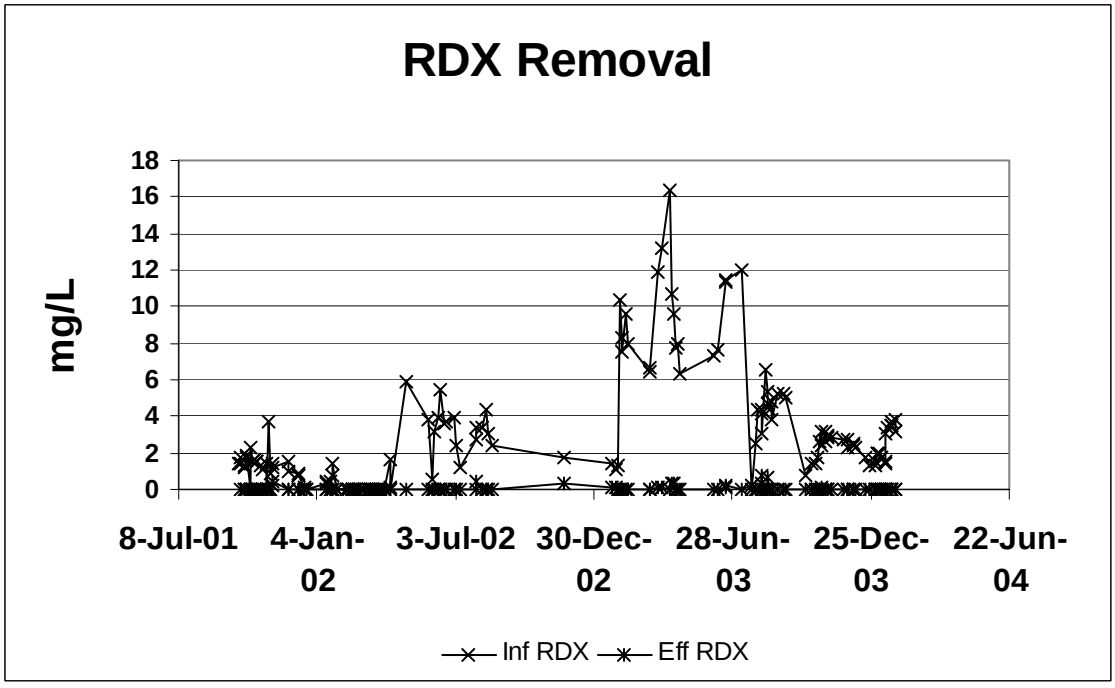

Figure 6. Influent and effluent RDX concentrations.

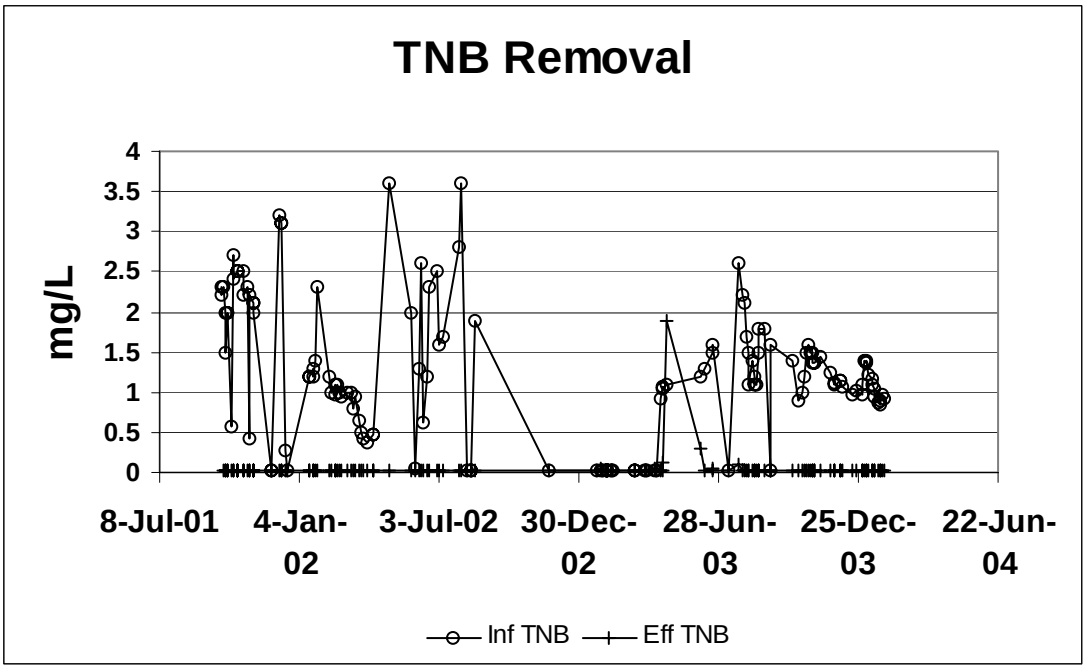

Figure 7. Influent and effluent TNB concentrations.

Table 3 summarizes all performance criteria used in the demonstration as reported in the Cost and Performance Report (ESTCP 2003). In addition to the parameters monitored and reported here, levels of BOD, nitrogen, and phosphorus were monitored at the WWTP. However, no deviations from normal were noted. As described above, the effluent flow from this demonstration was relatively small compared with the overall plant flow, and there was an intermediate holding pond for the wastewater. Time was ample, therefore, for the easily assimilated compounds such as excess ethanol and the reductively transformed by-products to mix and degrade to background levels in the wastewater collection system.

Ease of Use

The system initially provided a challenge to the operators at McAlester AAP due to the relative newness and complexity of the system, the use of highly automated controls, and problems with improper water level readings in the separator. These false readings caused repeated system shutdowns and frustrated the operators.

By the end of the operational period described in this report, however, the system had achieved a level of operation with which the personnel at McAlester AAP were comfortable. Once the problems with false water readings in the separator were solved, routine maintenance was all that was required. The routine maintenance primarily consisted of making up chemicals (macro and micro nutrients), replacing chemicals used as delivered (caustic and fuel grade ethanol), taking samples for

laboratory analysis, adjusting the control panel TNT concentration readout to the results of laboratory analysis, and backwashing the heat exchanger.

Influent Stream

TNT concentrations in the influent stream dramatically increased during the extended period of operation reported here. Concentrations up to 140 mg/L were observed, and concentrations around the value of 120 mg/L were observed for extended periods of time. The 120 mg/L reading represents a loading 50 percent greater than initial design. However, the exact value for loading in kg/m^3-day has not been extensively tested, and problems with the effluent transfer lines (which kept flow rates at 5 gpm or less late in the extended demonstration) yielded a loading rate that the process could handle.

Table 3. Performance and performance confirmation methods.

Performance Criteria	Expected Performance (pre-demo)	Performance Confirmation Method	Actual (post-demo)
Primary Criteria (Qualitative)			
Ease of Use	Same skill level as filter plant operator	Experience from demo	Additional troubleshooting required due to separator location
Primary Criteria (Quantitative)			
Cost/yr	<$19K	Cost of Consumables	$7.5K @ 5 gpm
Influent Stream – Flow Rate – Influent Conc.	7.5 gpm or greater 20-80 mg/L total nitrobodies	EPA Method 8330	Flow rates of up to 7.5 gpm tested. Maximum sustained rate of 6.0 gpm achieved. Influent concentration up to 140 mg/L
Target Hazardous Contaminant	< 100 μg/L total nitrobodies	EPA Method 8330	Met criteria 94% of time with no samples exceeding McAlester AAP limits
Process Waste	Wastewater suitable for discharge to aerobic WWTP 400 mg/L BOD, 45 mg/L ammonia	No adverse effect in existing WWTP	Criteria met – No measurable change in influent at existing WWTP after combination with other sources
Maintenance	Limited to reservoir replenishment during steady state operation	Observation and log book entries	Additional maintenance required due to separator and heater problems
Secondary Performance Criteria			
Spill Events	Depends on spill[1]	Rapid recovery of gas production from bacteria	No spill events occurred
Temperature and pH	Chemical and power use as predicted from pilot test	Comparison of usage to predictions	Use as predicted
Reliability	Operation without automatic shutdown periods	Observation from PLC logs	Separator and heater problems interfered with operations

[1] Spills do not refer to shock loadings. Influent TNT at the saturation limit does not pose a problem. Spills refer to other chemicals that may get into the pinkwater sumps. No known spills were experienced during the pilot test, and no spills will be simulated.

Target Hazardous Contaminants

The effluent limit for total nitrobodies (<100 μg/L) was met more than 95 percent of the time over the entire study period at the GAC-FBR. Table 3 included data only to August 2002. This report includes data to December 2003, so there are small differences between Table 3 (e.g., met nitrobodies criteria 94 percent) and this report, where the limit was met more than 95 percent of the time. The effluent limits at the WWTP were met 100 percent of the time. The primary difference is that the effluent from the GAC-FBR is small compared with the rest of the facility, and the process was applied to a high strength, low-flow wastewater. Once mixed with the rest of the plant flow, no violations of the National Pollutant Discharge Elimination System (NPDES) permit occurred.

Table 4 shows data acquired during a 6-week period in which operational problems did not occur with the mechanical operation of the system. During the period of stable operation shown in Table 4, no samples exceeded the 100 μg/L limit. Most of the samples that exceeded 100 μg/L total nitrobodies occurred during system upsets, and one occurred when the TNT concentration was not updated on the control screen (during a period of rapidly rising TNT concentrations). The latter condition caused too little ethanol and nutrients to be fed to the system to keep up with the TNT loading.

Table 4. Operating data from 23 September to 2 November 2003.

Date	Flow (gpd)	Influent TNT (mg/L)	TNT (kg/day)	TNT (kg/m^3-day)[1]
Design	**7.5**	**40**	**1.64**	**0.23**
23-Sep-03	6	127	4.15	0.58
08-Oct-03	5	97.7	2.66	0.37
15-Oct-03	5	97.7	2.66	0.37
20-Oct-03	3	96.1	1.57	0.22
22-Oct-03	5	98	2.67	0.37
23-Oct-03	6	90	2.94	0.41
27-Oct-03	3	102	1.67	0.23
28-Oct-03	2	94.9	1.03	0.14
31-Oct-03	3.8	93.4	1.93	0.27
02-Nov-03	4.5	95.1	2.33	0.32
Weighted Average	4.5	95	2.53	0.37

[1] Loading in kg of TNT, per cubic meter of reactor bed volume, per day

Process Waste

One of the concerns expressed at the outset of the study was related to increasing the nutrient loading on the existing WWTP. The GAC-FBR process would add biodegradable materials, as well as nitrogen and phosphorus, to the wastewater collection system. To determine whether this additional load could be handled by the existing wastewater system, records were analyzed to determine to what extent the nutrient load increased, and whether the plant could handle any increased load. No noticeable increases were observed in the influent quality at the WWTP.

Figure 8 shows the WWTP effluent ammonia values for the McAlester AAP WWTP starting from before the ESTCP demonstration until the end. Differences in the effluent values were not noticeable, and no permit violations occurred during the period. The first peak in concentration shown, which represents August 1999, occurred before the demonstration began. According to McAlester AAP personnel, this corresponds to a period when major maintenance was being performed on the WWTP. The second peak, which represents February 2002, did occur during the demonstration period, but the variations observed during the entire data record show that this is not substantially out of the ordinary.

The values of the second peak of ammonia concentration occurred when the TNT concentration in the influent was relatively low. During the February 2002 timeframe, the TNT concentration was averaging about 10 mg/L. This means that the contribution from the GAC-FBR would also be at a low point, because all of the nutrient feeds are pegged to the TNT influent concentration. Thus, the two nutrient solutions fed to the GAC-FBR would have been at their lowest point when the second peak of ammonia concentration occurred during the February 2002 period. Therefore, the peak in the ammonia concentration is not attributable to the GAC-FBR operation.

TNT influent concentrations were compared with the ammonia effluents for the entire demonstration period to determine if there were any trends or correlations to be found. This comparison can be seen by comparing Figures 8 and 9, where the TNT influent concentration, in mg/L, is plotted over the same timeframe as the ammonia data. There is no correlation and, in fact, when the TNT concentrations were greatest (at the end of the demonstration period), the ammonia concentrations were lowest. Based on this, it is concluded that the GAC-FBR will not place unacceptable loads of nutrients on the WWTP. Although the effluent from the GAC-FBR is high in ammonia, the flow rate is low compared to the total wastewater generated at McAlester AAP, and the contribution from the GAC-FBR is negligible.

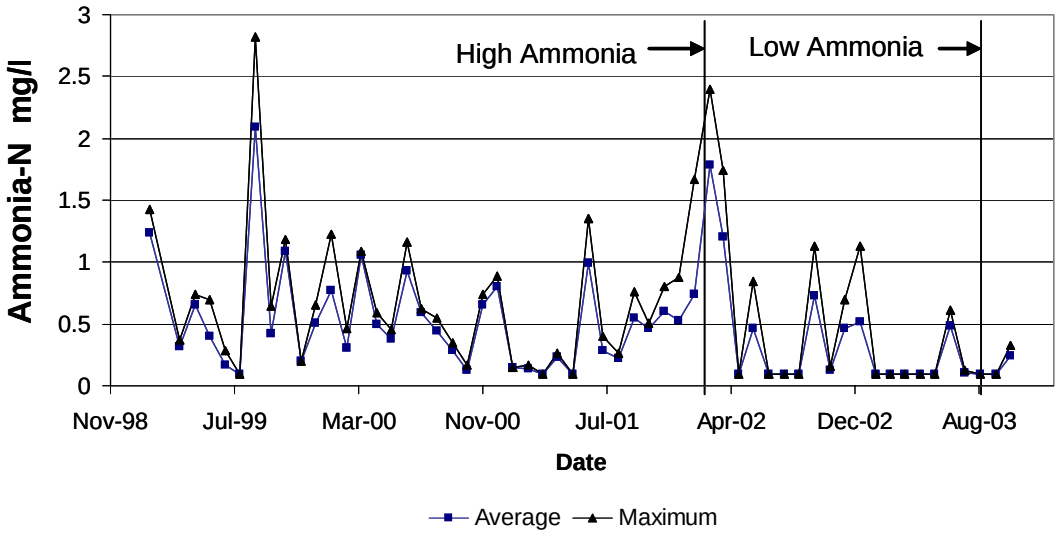

Figure 8. Ammonia levels in McAlester AAP wastewater effluent.

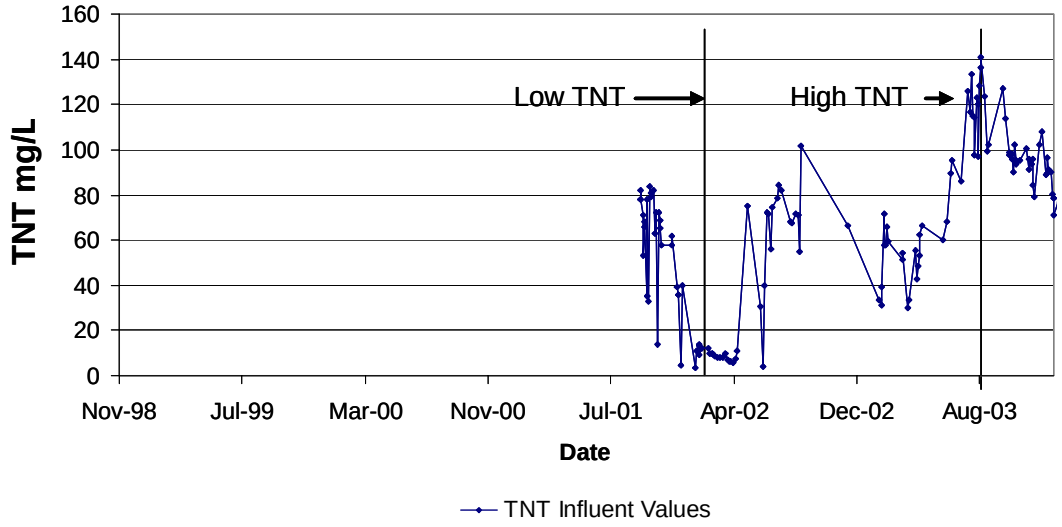

Figure 9. Comparison of WWTP ammonia effluent to GAC-FBR influent TNT.

Maintenance

The maintenance record for the GAC-FBR improved substantially after the problem with the false readings on the separator was identified and circumvented. During the final 5 months of operation, the only extraordinary maintenance item resulted from the failure of the temperature controller on the main heater. This failure was identified and the controller replaced by McAlester AAP personnel.

Spill Events

No spill events are known to have occurred on the bioplant during the demonstration. A spill of a cleaning solution called Simple Green definitely occurred on the existing plant, causing problems at the GAC adsorption plant and significantly reducing the service time for a batch of GAC. It is not known whether the spill also made it into the GAC-FBR, because the influent tanks were filled on a batch basis, and the batch fills may have occurred outside the timeframe that Simple Green hit the existing plant. However, no effect was seen on the GAC-FBR at the time problems were seen on the GAC adsorption plant.

Temperature and pH

The chemical and power use were as predicted from the pilot study. The use of caustic addition to control pH may have been slightly less than during the pilot study, but in both cases was very low. Power was not possible to quantify at the demonstration site, but the heater was able to maintain temperature. Temperature problems did occur, but were related to fuses blowing on the temperature controller. The causes of the fuse problem was never determined, although representatives from the vendor (Watlow, St. Louis, MO) said they had observed similar problems with systems in which the wiring from the heater to the fuse was less than 10 feet (as in our application). The vendor suggested that heat was being transferred through the wire back to the fuse, degrading its ability to carry the load. The fuses were 15 amp each, and the anecdotal evidence from the demonstration supports this theory, because fuses only blew during the summer when there would have been less heat loss from the wire to the surrounding air.

Reliability

The reliability of the reactor continued to be a problem until the last 6 months of the operation. After the problems with vapor lock in the air lines and associated false readings from the water level in the separator were identified, the reactor operated without significant problems.

7 Cost Comparison

The cost comparison presented here deals primarily with the use of ethanol, the main cost driver in the operations of the GAC-FBR. The amounts required for power and heat are taken from the cost estimates used in the ESTCP proposal. These amounts are based on engineering estimates for the pumps and heating required, and rely on vendor projections as well as conditions expected at the site (e.g., average and minimum water temperatures).

The cost comparison also leaves out a capital cost for the GAC adsorption system. There are several reasons for this. First, the authors believe that the total cost (capital and operations and maintenance [O&M] costs) of a new GAC-FBR would be less than the O&M costs of the existing system. Second, the GAC plant was already in place; therefore, no capital costs would be expended at the site chosen for demonstration. Lastly, the system as built at McAlester AAP is unlikely to be duplicated elsewhere because simpler methods for particulate removal have been developed. McAlester AAP uses flocculation, settling, and pressure filtration prior to the carbon filters, whereas Milan AAP accomplishes the same particulate removal using a membrane process.

The main purpose here is to determine if the GAC-FBR is more cost effective than the continued operation of the existing system, and to get the best possible estimate of the main cost driver – the ethanol used as substrate for the micro-organisms.

The original cost estimates for operation of the GAC-FBR are shown in Table 5. These estimates represent the values that were used during the proposal process for ESTCP. These estimates are based on an average TNT concentration of 40 mg/L and a flow of 7.5 gpm. The design criteria and underlying assumptions for the cost estimates are shown in the Appendix.

Table 5. Cost estimtes for GAC-FBR from ESTCP proposal.

Category	Annual Cost ($)
Power	3,400
Heat	2,400
Ethanol	10,600
Nutrients	600
pH control	1,700
Amortized capital costs	17,000
Total	**35,700**

The costs will be compared here based on historical GAC usage at McAlester AAP and actual costs observed for the GAC-FBR. The costs for the existing process were based solely on the disposal of carbon from the 2-yr period during which the pilot test was conducted. During that period, 64,170 lb/yr of GAC had been disposed of. Further data were analyzed, showing that over the previous 4 years (from the pilot study) representing 1996-1999, average disposal of GAC was 64,342 lb/yr, so this value appeared fairly constant over that period. The GAC cost was $1.12/lb (purchase and disposal combined), yielding an annual cost of $71,000 for the existing system based solely on consumed GAC. In addition, manpower is needed to remove and replace GAC in the columns, and place the spent GAC in drums for disposal. McAlester AAP estimates that removing, replacing, and drumming GAC from one column requires 37.5 man-hours. The GAC usage rate for McAlester AAP was approximately 64,000 lb/yr, which required 14 change outs at 4,500 lb of GAC per column. The labor cost for 14 change outs is estimated to be (based on 37.5 hr per change out at $68.24/hr) $35,800, making the total annual cost for GAC adsorption $106,800. Separate estimates for purchase and disposal of GAC were not made.

One of the principal problems in cost estimating during the periods involving operational problems is that ethanol is consumed, but pinkwater is not being treated. This practice is referred to as "warm shutdown," because the system is not shut off, but is not taking new flow due to problems such as an overflow in the effluent transfer barrel, pH values out of range, low temperature on the reactor, etc.

During the period represented by Table 5, approximately 350 kgal of pinkwater was treated. Ethanol consumption was seven 55-gal barrels, yielding an ethanol cost of approximately $3.90/kgal of pinkwater treated (see Table 6), or approximately $10,000/yr.

Table 6 shows the calculations used to arrive at the $10,000/yr estimate. A design flow of 5 gpm is used in this calculation because it maintains the mass loading in kg TNT per cubic meter of reactor bed at 0.37, which is between the design values of 0.22 (average) and 0.51 (maximum) used in the development of the GAC-FBR. The data in Table 4 show that the design maximum was occasionally exceeded. As discussed previously, the main design component for the GAC-FBR is the mass loading, which is derived from the influent flow rate and the TNT concentration in the influent. During the pilot study (Maloney et al. 2002), the influent concentration ranged from 20 to 80 mg/L, and averaged 40 mg/L. During the period represented in Table 5, the TNT concentration averaged 95 mg/L, resulting in a greater demand for ethanol.

The actual cost for ethanol usage derived from the Cost and Performance Report (ESTCP 2003) was $8,800/yr. The original cost estimate for the project was

$10,600/yr, which was based on continuous smooth operation of the system at an average of 40 mg/L TNT and 7.5 gpm flow. Although the original estimate was higher, the lower actual usage was not unexpected because of operating problems during the demonstration. The data in Table 6 represent actual cost numbers for a period without operating problems, except that the flowrate could not be maintained at 7.5 gpm. Thus, although the cost estimate in Table 6 compares favorably with that in Table 5 (the original estimate, $10,600), it is based on a flowrate that is only two-thirds of the original planned flowrate. It should follow that the actual cost in Table 6 would be about two-thirds of that shown in Table 5.

The reason for the higher cost for the period in Table 4 is the higher TNT concentrations encountered during this period. During the first portion of this study, the TNT concentration averaged less than 40 mg/L. The ethanol feed rate is proportional to the TNT concentration, because it represents the primary demand for substrate. During the period represented in Table 5, the weighted average of the TNT concentration was 95 mg/L. The cost of consumables should increase by the ratio of the TNT concentrations, which would yield about $18,000/yr. Thus, the system used ethanol more efficiently during the period represented in Table 5, but the higher TNT concentration caused ethanol to be used at a greater daily rate.

Table 6. Ethanol usage and cost at high TNT concentrations.

Ethanol usage during period (barrels)	7.00
Gallons Ethanol during period (gal)	385
Ethanol cost at $3.47/gal ($)	1335.95
Pinkwater treated (kgal)	346
Ethanol cost, $/kgal of pinkwater	3.87
Kgal/yr at 5 gpm	26,280
Cost/yr at 5 gpm ($K)	**$10.16**

Therefore, the period of stable operation did yield a lower cost of consumables when represented in $/kg TNT treated. The amount also remained less than the original cost estimate ($19,000/yr), and very close to the original estimate for ethanol costs shown in Table 3 ($10,600/yr). This amount still represents the bulk of the operating cost and is closely tied to the cost of ethanol purchased. This study was conducted with ethanol purchased at $3.47/gal. Fuel grade ethanol can be purchased at lower levels, but plant operating practices did not allow the storage of large quantities of fuel grade ethanol, and lower prices are available only on larger bulk deliveries.

If the flow rate was increased to 7.5 gpm, the ethanol cost would increase to $15,000/yr, based on the data in Tables 5 and 6. It is questionable whether this reactor could treat a sustained load of 95 mg/L TNT at 7.5 gpm, which results in a mass loading of 2.5 times the original design (0.55 vs. 0.22 kg/m^3-day). In addition

to the difference in ethanol cost from Table 4, a higher amortized cost for the reactor was shown in the demonstration. The original estimate for capital equipment was $195,000. However, construction problems and the addition of a complete enclosure for the fluidized bed added an additional $95,000 to the project, for a total of $290,000. The total $290,000 for unit purchase, installation, and construction problems has been treated as capital cost for this analysis. The amortized capital cost (6 percent, 20 years) for the GAC-FBR is $25,300/yr.

Lastly, the labor cost for the GAC-FBR needs to be included for a direct comparison to the existing system. Operational problems caused the labor demands at the GAC-FBR to be greater than originally estimated and greater than the labor required for carbon changeouts. Based on the data from the demonstration, 744 hr of labor at $68/hr was used, for a total of $50,770 annually. The revised costs for the GAC-FBR, and the comparative costs for the existing system, are shown in Table 7.

Based on this comparison, a new GAC-FBR is only slightly less expensive than the O&M for an existing GAC adsorption system. However, on an operating cost basis (i.e., remove the amortized capital costs), it is at least 30 percent less expensive. Further, no operational costs were assigned for the GAC adsorption system, which does require manual start and stop, as well as maintenance on the pressure filters and settling basins. The anaerobic GAC-FBR was fed water directly from the influent basin, bypassing the coagulation, settling, and pressure filtration operations, therefore avoiding the costs of operating these three processes. However, there is no good estimate of the cost for operating these systems, so it is left out of the analysis.

Table 7. Cost comparisons.

Category	GAC-FBR Annual Cost ($)	GAC Adsorption ($)
Power	3,400	?
Heat	2,400	?
Ethanol	15,000	NA
Nutrients	600	NA
pH control	1,700	NA
Labor cost	50,800	35,800
Spent carbon replace/dispose		71,000
Total O&M costs	73,900	106,800
Amortized capital costs	25,300	Unknown
Total[1]	**$ 99,200[2]**	**$106,800[3]**

[1] Includes capital and O&M costs
[2] Includes only O&M costs
[3] Compares cost of new system to existing O&M

8 Conclusions and Recommendations

The demonstration of near full-scale anaerobic GAC-FBR for the treatment of pinkwater at McAlester AAP was a success. The system was more expensive than initially estimated due to operational problems that required much higher labor hours. Most of these problems were solved by the end of the demonstration, and the requirement for labor hours should be reduced to the amount required for operation of the adsorption system (not including the labor required to remove and replace spent carbon).

A new GAC-FBR had a total cost for capital and O&M less than just the O&M costs of the existing system. Costs for power and heat at the existing system could not be determined in the field, so they were left at zero in the comparison. However, there clearly would be some cost for the pumps and building heat in the existing GAC adsorption plant. O&M costs were 30 percent less for the GAC-FBR than for the existing system even after some costs for the existing system were left out. The GAC-FBR does not require capital costs for a filtration system as required for the GAC adsorption system. Therefore, the overall costs for a GAC-FBR should be significantly less than conventional GAC adsorption when a totally new installation is required.

The GAC-FBR proved to be equally capable of treating pinkwater when compared with a conventional GAC plant. The system did not generate any hazardous waste for disposal during the 3 years it operated, thus reducing the Army's generation of hazardous waste.

This system operated for approximately 3 years, with no replacement of carbon required. Further, it proved to be a much more robust system in terms of handling upsets and cold shutdowns than was expected. The flexibility of the system is suitable for industrial applications.

The costs were higher than originally estimated, due to the many operational problems encountered, but these systems should evolve to more easily operated modes as more experience is gained. The experience with a similar system at Albany International Airport shows that semi-automatic operation can be achieved. The only additional component of the McAlester AAP system compared to Albany was the ethanol

co-substrate feed system. However, Albany's system did not start with the reactor and the separator on two different hydraulic grade lines.

The anaerobic GAC-FBR should be considered for new installations of pinkwater treatment where secondary treatment of the effluent is available. This should always be done as a cost comparison to conventional GAC adsorption, which may also force GAC adsorption service providers to lower their prices to compete in an open setting where more than one system is available to meet treatment requirements.

Lastly, the anaerobic GAC-FBR is also applicable to treatment of oxidized compounds that are not adsorbable. Ammonium picrate, or Yellow D as it is commonly known, is an energetic compound used by the military that is not well adsorbed and could not be removed by GAC adsorption. New compounds such as ammonium perchlorate, which are now being introduced into high explosive mixtures, also fit into this category.

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Appendix: Excerpts From Original ESTCP Proposal–Design Criteria

Design Criteria for Anaerobic GAC-FBR Treatment of Pinkwater at McAlester AAP

TNT Concentration (mg/L)	
Average	39.0
Maximum	84.8
TNT Loading Rate (kg/m^3-d)	
Average	0.22
Maximum	0.51
Feed Flow Rate* (gpm)	
Average	7.5
Maximum	16.8

*Assumes daily operation for 7 days per week

Reactor Design

Size	(feet)
Diameter	4.5
Bed Height	16.0
Reactor Height	22.0
TNT Loading Rate	**(kg/m^3-d)**
Average TNT Concentration Average Flow Rate	0.22
Average TNT Concentration Maximum Flow Rate	0.48
Maximum TNT Concentration Average Flow Rate	0.49

Operating Cost Elements of Anaerobic Treatment System

- Electron Donor (ethanol)
- Nutrients
- pH Control (caustic)
- Power
- Heating
- Manpower

Electron Donor (Ethanol) Costs

- Assume COD/TNT (average) of 27.5
- Influent COD = 1075 mg/L
- Influent Ethanol = 515 mg/L
- Daily Usage = 6.95 gallons/day
- Ethanol Cost (fuel grade) = $1.60/gallon
- Cost during pilot @ Central Garden & Pet = $4.18/gallon
- Annual Cost = $4,058/year to $10,606/year

Summary of Chemical Costs

Nutrient Source	lb./month	cost/lb.	cost/month
Urea (N)	71.9	$0.202	$14.52
DAP (P)	28.0	$0.730	$20.41
Trace Minerals	--	--	$15.00

- Nitrogen and phosphorus requirements based on biomass yield of 10%
- Trace metals added as pulse 2X/week

Summary of Power Costs

Pump Designation	hp	Cost ($/d)
Fluidization Pump	7.5	8.05
Growth Control/Media Return	0.5	0.54
Nutrient Feed	0.25	0.27
Caustic Feed	0.25	0.22
Ethanol Feed	0.25	0.22
Total	8.75	9.35
		($3,413/year)

Power cost of $0.06/kwh used

Cost of pH Control

- Usage = 1.85 gallons of 15% NaOH per day for 1.5 gpm
- Usage of NaOH @ 7.5 gpm calculated to be 338 gallons of 20% NaOH
- Cost per year @ $2.08/gallon = $702/year

Summary of Heating Costs

- Average Feed Water Temperature 60°F
- Minimum Feed Water Temperature 40°F
- Operating Temperature 90°F
- Heat from Fluidization Pump 3°F
- Btu Required (Btu/day) 1.71×10^6
- Heat Transfer Efficiency 65%
- Cost of Btu's $2.5/MM Btu
- Annual Cost $2,400/year

Summary of Operating Costs

Item	Annual Cost ($/year)
Power	$3,413
Heat	$2,400
Ethanol ($4.18/gallon)	$10,606
Nutrients	$599
pH Control	$702
Total	$17,720

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14. ABSTRACT

This report documents a demonstration project conducted at McAlester Army Ammunition Plant in Oklahoma. The technology is based on anaerobic bacteria which attack dissolved explosives such as TNT and RDX at the nitro groups, converting them to amino groups. Once the explosives are transformed, they become amenable to aerobic degradation. This process functions as a pretreatment for the pinkwater, after which the effluent is discharged to an aerobic treatment plant and mixed with the rest of the plant's wastewater. The bacteria are cultivated on granules of activated carbon contained in a fluidized bed. The demonstration equipment controlled the conditions to maintain favorable conditions for anaerobic bacteria through control of temperature, pH, and nutrients. Fuel grade ethanol was used as the substrate to maintain the bacterial population. The results show that this technique can be successful and less costly than the existing granular activated carbon adsorption process.

15. SUBJECT TERMS

biodegradation	McAlester, OK	hazardous waste management
Army Ammunition Plant (AAP)	demilitarization	pinkwater, wastewater treatment

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